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⑦③ Proprietor : **MINNESOTA MINING AND
MANUFACTURING COMPANY**
3M Center, P.O. Box 33427
St. Paul, Minnesota 55133-3427 (US)

⑦② Inventor : **Scholz, Matthew T. c/o Minnesota
Mining and
Manufacturing Co. 2501 Hudson Road P.O.
Box 33427
St. Paul Minnesota 55133-3427 (US)**
Inventor : **Birkholz, Russell D. c/o Minnesota
Mining and
Manufacturing Co. 2501 Hudson Road P.O.
Box 33427
St. Paul Minnesota 55133-3427 (US)**

⑦④ Representative : **Baillie, Iain Cameron et al
c/o Ladas & Parry, Althelmer Eck 2
W-8000 München 2 (DE)**

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Description**ORTHOPEDIC SPLINTING AND CASTING ARTICLE**

5 Splinting and casting articles for orthopedic purposes such as immobilization of body parts typically are constructed from porous fabrics that are coated or impregnated with plaster of paris or curable resins. Most of the curable resin systems and the plaster of paris systems are cured or rigidified by exposure to water or aqueous catalyst systems.

Once applied to the patient an effective orthopedic article must provide sufficient strength to protect the immobilized body part. It is also desirable that it be light weight, easy to apply, resistant to degradation due to environmental conditions, particularly water, relatively fast and convenient to cure and sufficiently breathable to allow good oxygen transport and transmission of volatile materials from the skin.

When using orthopedic articles systems which are cured by water or water activated catalysts, it is desirable and necessary to allow ready access to the casting system by water in order to obtain both rapid and complete cure. On the other hand, it is desirable that once cured, the orthopedic article dry as rapidly and completely as possible and be relatively insensitive to water, so as to allow bathing and discretionary exposure to water. It is also desirable that the dried orthopedic article provide improved breathability and porosity to minimize the exposure of the skin under the cast to a continuing moist environment.

20 The present invention provides for the first time a unitary, ready to apply splinting or casting article which combines the advantages of a porous exterior covering layer and yet protects the skin from leakage of the resin impregnated into the casting material.

The present invention provides an improved orthopedic splinting or casting article which cures rapidly and which has an exterior covering layer. The exterior covering layer has a low surface energy and a porosity sufficient to be breathable while not allowing leakage of its contents. The low surface energy exterior is provided by treatment of the exterior layer of the article, with, for example, a suitable chemical such as a fluorochemical or a silicone. The orthopedic article is constructed of a flexible or moldable substrate that is impregnated with a compound that cures the substrate into an inflexible, load-bearing surface. In the context of this application, "a flexible substrate that is impregnated with a curable compound" is equivalent to "a casting material". Preferably, the article is unitary and comprises a water activated resin-impregnated structural member and a porous exterior covering layer. The cure rate of the resin-impregnated structural member can be adjusted to be faster or slower, while providing improved breathability and improved water-repellency to the article.

In general, casting materials currently available which are constructed of resins impregnated into a sheet comprise resins with surface tensions lower than water. The surface tension of the exterior surface of the orthopedic article of this application is significantly lower than water and known resins and, therefore, the article is water repellent.

It is also an object of the invention to provide a very porous orthopedic splinting or casting article with improved handleability, e.g., which may be handled without protective gloves. The casting resin is enclosed by a low surface energy exterior layer having a porosity that provides excellent containment of the resin before cure. This means that the liquid curable resin does not migrate through the porous exterior covering layer, thereby providing an article with improved storage stability.

Figure 1 shows a casting system 1 of the invention wherein a low surface energy layer 2 surrounds a resin-impregnated member 3.

Figure 2 shows a casting system 1 wherein a resin-impregnated laminate 4 is sealed at the laminate ends 5 and 6 to provide complete enclosure.

45 Figure 3 shows a system wherein a foam layer 7 is applied to one surface 8 of the casting system 1.

Figure 4 shows a system wherein a film layer 9 is applied to the surface 2 of a casting system 1.

Figure 5a shows a casting splint formed into a semicylinder to be prepared for a porosity test.

Figure 5b shows the splint of Figure 5a formed into a complete cylinder.

Figure 6 shows a tubular casting article 15. Cylinders 16 and 18 are covering layers with low surface tension. A casting material is contained between the covering layers.

Figure 7 shows schematically the article of Figure 6 folded for storage.

Figure 8 shows water transport through treated and untreated orthopedic articles in grams per day.

This application relates to an improved porous orthopedic splinting and casting article and a method for imparting oil and water repellency to such articles. This application also relates to strong and light-weight orthotic devices with excellent porosity and stability.

55 In the method of the present invention oil-repellency and water repellency is imparted to casting articles by a chemical treatment which provides low surface energy to the exposed surface of the article. It has been found that this can be done with articles having very high porosity without inhibiting adequate cure since such

articles require exposure to an aqueous environment to effect a cure.

As shown in Figure 1, the orthopedic article of this application generally consists of a flexible substrate 3 that is impregnated with a liquid curable compound, and a water-permeable envelope 2 that surrounds the substrate. Suitable envelopes include water-permeable microporous woven, knitted, non-woven or melt blown layers such as weft knitted tubular fabric, knitted stockinet, non-woven polymeric webs of many types such as polyesters, polyurethanes, nylons or polyolefins, foams, various natural and synthetic woven fabrics such as cotton or synthetic polymeric fabrics such as polyesters, and nylons, including spun laced fabrics. These materials may be of high or low modulus but are preferably in a configuration which facilitates conformability and should therefore be drapable, and preferably extensible. The covering material may also be heat sealable.

Water-permeable materials as used herein refer to materials having porosity to both water vapor and liquid.

Suitable fluorochemicals for use to obtain low surface energy layers include any of the fluorochemicals known to those skilled in the art to provide oil-repellency and optionally water repellency to natural or synthetic fibers and films. In general, fluorochemical agents or compositions useful in this invention comprise fluorochemical compounds or polymers containing fluoroaliphatic radicals or groups, Rf.

The fluoroaliphatic radical, Rf, is a fluorinated, stable, inert, non-polar, preferably saturated, monovalent moiety which is both hydrophobic and oleophobic. It can be straight chain, branched chain, or, if sufficiently large, cyclic, or combinations thereof, such as alkylcycloaliphatic radicals. The skeletal chain in the fluoroaliphatic radical can include catenary divalent oxygen atoms and/or trivalent nitrogen atoms bonded only to carbon atoms. Generally Rf will have 3 to 20 carbon atoms, preferably 6 to 12 carbon atoms, and will contain 40 to 78 weight percent, preferably 50 to 78 weight percent, carbon-bound fluorine. The terminal portion of the Rf group has at least one trifluoromethyl group, and preferably has a terminal group of at least three fully fluorinated carbon atoms, e.g., $\text{CF}_3\text{CF}_2\text{CF}_2^-$. The preferred Rf groups are fully or substantially fluorinated, as in the case where Rf is perfluoroalkyl, $\text{C}_n\text{F}_{2n+1}^-$. Classes of fluorochemical agents or compositions useful in this invention include compounds and polymers containing one or more fluoroaliphatic radicals, Rf. Examples of such compounds include, for example, fluorochemical urethanes, ureas, esters, amines (and salts thereof), amides, acids (and salts thereof), carbodiimides, guanidines, allophanates, biurets, and compounds containing two or more of these groups, as well as blends of these compounds.

Useful fluorochemical polymers containing Rf radicals include copolymers of fluorochemical acrylate and/or methacrylate monomers with co-polymerizable monomers, including fluorine-containing and fluorine-free monomers, such as methyl methacrylate, butyl acrylate, octadecyl methacrylate, acrylate and methacrylate esters of poly(oxyalkylene) polyol oligomers and polymers, e.g., poly(oxyethylene) glycol dimethacrylate, glycidyl methacrylate, ethylene, vinyl acetate, vinyl chloride, vinylidene chloride, vinylidene fluoride, acrylonitrile, vinyl chloroacetate, isoprene, chloroprene, styrene, butadiene, vinylpyridine, vinyl alkyl esters, vinyl alkyl ketones, acrylic and methacrylic acid, 2-hydroxyethyl acrylate, N-methylolacrylamide, 2-(N,N,N-trimethylammonium) ethyl methacrylate and the like.

The relative amounts of various comonomers which can be used with fluorochemical monomer will generally be selected empirically, and will depend on the substrate to be treated, the properties desired from the fluorochemical treatment, i.e., the degree of oil and/or water repellency desired, and the mode of application to the substrate.

Useful fluorochemical agents or compositions include blends of the various classes fluorochemical compounds and/or polymers described above. Also, blends of these fluorochemical compounds or polymers with fluorine-free compounds, e.g., N-acyl aziridines, or fluorine-free polymers, e.g., polyacrylates such as poly(methyl methacrylate) and poly(methyl methacrylate-co-decyl acrylate), and polysiloxanes.

The fluorochemical agents or compositions can include non-interfering adjuvants such as wetting agents, emulsifiers, solvents (aqueous and organic), dyes, biocides, fillers, catalysts, curing agents and the like.

The final fluorochemical agent or composition should contain, on a solids basis, at least 5 weight percent, preferably at least 10 weight percent carbon-bound fluorine in the form of said Rf groups in order to impart the benefits described in this invention.

Such fluorochemicals are generally known and commercially available as perfluoroaliphatic group bearing water/oil repellant agents which contain at least 5 percent by weight of fluorine, preferably 7 to 12 percent of fluorine in the available formulations.

As specifically known formulations, the following examples are named:

By the reaction of the perfluoroaliphatic thioglycols with diisocyanates, there results perfluoroaliphatic group-bearing polyurethanes. These products are normally applied in aqueous dispersion for fiber treatment. Such reaction products are e.g. described in U.S. Patent No. 4,054,592.

Another group of suitable compounds are perfluoroaliphatic group-bearing N-methylol condensation products. These compounds are described in U.S. Patent No. 4,477,498, where the emulsification of such products is dealt with in detail.

The perfluoroaliphatic group-bearing polycarbodimides are, e.g., obtained by reaction of perfluoroaliphatic sulfonamide alkanols with polyisocyanates in the presence of suitable catalysts. This class of compounds can be used by itself, but often is used with other R_F-group bearing compounds, especially with (co)polymers. Thus, another group of compounds which can be used in dispersions is mentioned. Among these compounds all known polymers bearing fluoroaliphatic residues can be used, also condensation polymers, such as polyesters and polyamides which contain the corresponding perfluoroaliphatic groups, are considered but especially (co)polymers on the basis of e.g. R_F-acrylates and R_F-methacrylates, which can contain different fluorine-free vinyl compounds as comonomers. In DE-A 2 310 801 (see also GB-A 1.413.051/052), these compounds are discussed in detail. The manufacture of R_F-group bearing polycarbodimides as well as the combination of these compounds with each other is also described in detail.

Besides the aforementioned perfluoroaliphatic group-bearing agents, further fluorochemical components may be used, for example, R_F-group-bearing guanidines, U.S. Patent No. 4,540,479, R_F-group-bearing allophanates, U.S. Patent No. 4,606,737 and R_F-group-bearing biurets, U.S. Patent No. 4,668,406. These classes are mostly used in combination. Others include fluoralkyl-substituted siloxanes, e.g.,

$\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$.

The useful compounds show, in general, one or more perfluoroaliphatic residues with preferably at least 4 carbon atoms, especially 6 to 14 atoms each.

An exemplary preferred fluorochemical is a formulation of 70% solvents and 30% emulsified solid fluorochemical polymers. The formulation includes as solvents 11% methyl isobutyl ketone, 6% ethylene glycol and 53% water. The fluorochemical polymers are a 50/50 blend of 5/95 copolymer of butyl acrylate and $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_3)\text{C}_2\text{H}_4\text{OCOCH}=\text{CH}_2$ prepared as described in U.S. Patent 3,816,229 (see particularly column 3, lines 66-68 and column 4, lines 1-11) for a 10/90 copolymer. The second component of the 50/50 blend is a copolymer prepared from 1 mole of a tri-functional phenyl isocyanate (available from Upjohn Company under the name PAPI), 2 moles of $\text{C}_8\text{F}_{17}\text{N}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$ and 1 mole of stearyl alcohol prepared as described in U.S. Patent 4,401,780 (see particularly Table I, C2 underfootnote A). Emulsifiers used are conventional commercially available materials such as polyethoxylated quaternary ammonium compounds (available under the name 5% Ethoquad 18/25) and 7.5% of a 50/50 mixture of $\text{C}_8\text{F}_{17}\text{SO}_2\text{NHC}_3\text{H}_6\text{N}(\text{CH}_3)_3\text{Cl}$ and a polyethoxylated sorbitan monooleate (available from ICI Limited under the name Tween 80). Such fluorochemicals are non-yellowing and particularly non-irritating to the skin as well as providing articles that are stable having excellent long term aging properties.

Exemplary fluorochemicals are available commercially from the 3M Company and include ready to use formulations such as Scotchgard™ Fabric Protectors FC-214 and FC-270, Scotch-Release™ Brand Fabric Treatment FC-248, Scotchgard™ Brand Fabric Protector FC-324, 3M™ Brand Textile Chemical FC-461, 3M™ Brand Textile Chemical FC-210, 3M™ Brand Textile Chemical FC-828, 3M™ Brand FC 393, FC 326, FC 905 and FC214B, and Scotchgard™ Brand Rain and Stain Repeller FC-232. Other commercially available materials include Dupont's Soil Shedd™ (available from duPont de Nemours and Company, Wilmington, Delaware).

Suitable silicones for use to obtain the low surface energy layers of the instant invention include any of the silicones known to those skilled in the art to provide water repellency and optionally oil repellency to fibers and films. Silicone fluids typically consist of linear polymers of rather low molecular weight, namely about 4000-25000. Most commonly the polymers are polydimethylsiloxanes.

For use as fluids with enhanced thermal stability, silicones containing both methyl and phenyl groups are used. Generally, the phenyl groups make up 10-45% of the total number of substituent groups present. Such silicones are generally obtained by hydrolysis of mixtures of methyl and phenylchlorosilanes.

Fluids for use in textile treatment may incorporate reactive groups so that they may be cross-linked to give a permanent finish. Commonly, these fluids contain Si-H bonds (introduced by including methylchlorosilane in the polymerization system) and cross-linking occurs on heating with alkali.

Examples of suitable silicones are those available from Dow-Corning Corporation such as C2-0563 and from General Electric Corporation such as GE-SS4098.

The fluorochemical or silicone which is added to water permeable envelope 2 to impart low surface energy is generally applied at low levels. Suitable amounts are between 0.001 to 0.10 parts by weight of active ingredient per part of fabric or padding. A preferred range is 0.25 to 5.0% by weight, i.e., 0.0025 to 0.050 grams of active ingredient per gram of the envelope.

The curable compound used for impregnating the flexible substrate can be any of the curable compounds known for use in orthopedic applications. Suitable curable compounds include plaster of paris and water-curable prepolymers of polyurethanes, cyanoacrylate esters, and epoxy resins. Particularly preferred curable compounds are isocyanate-terminated prepolymers, which are contained in Scotchcast™2 Brand casting tape.

In the embodiment shown in Figure 2, flexible substrate 4 is composed of a plurality of sheets or webs that are impregnated with a curable compound. Also shown in Figure 2, ends 5 and 6 of envelope 2 are sealed to

create a unitary, self-contained orthopedic article. It is also possible and usually preferred to seal the sides of the envelope.

In the embodiment shown in Figure 3, a foam layer 7 is applied to one surface of envelope 2. Foam layer 7 is adapted to contact the body part to be immobilized. That is, foam layer 7 acts as a cushion between the body part to be immobilized and member 3. Alternatively a treated foam layer can be included inside the treated fabric envelope.

In the embodiment shown in Figure 4, an impermeable film 9 is provided on one surface of envelope 2. In some instances, it is desirable to keep a surface of the orthopedic article relatively dry. For example, applying a wetted orthopedic article to the area of the body to be immobilized may interfere with medical compositions that have been applied to the body. Impermeable film 9 is provided in order to keep the underlying surface of envelope 2 dry when the orthopedic article is immersed in water to initiate cure.

Splints or casts may partially or totally encompass the body part to be stabilized and protected, and the ends of the splinting article may be joined to form a cylinder, as shown in Figure 5b. Preformed tubes, such as shown in Figure 6, are also contemplated in the instant invention.

A further embodiment contemplated is a resin impregnated sheet enclosed between 2 pieces of open cell foam wherein the foam and/or an adhesive covering one side of the foam is fluorochemically treated.

Various other constructions of articles can be made. There are far too many possibilities available to illustrate them all. The essential element will always be an envelope that possesses a low surface energy and a sufficient porosity to be breathable, yet which contains the casting material without allowing resin leakage.

The method for measuring the surface energy is AATCC Test Method 118-1983, with the modifications described below. Surface energies measured according to this modified test method are hereinafter referred to as "apparent" surface energies. AATCC test method 118-1983 determines the surface energy of a fabric by evaluating the fabric's resistance to wetting by a series of selected hydrocarbon compositions. The hydrocarbons set forth in AATCC 118-1983, however, only provide for measurements of surface energy from about 19.8×10^{-3} to 27.3×10^{-3} N/m (19.8 to 27.3 dynes per centimeter) at 25°C. This range is extended by employing various mixtures of methanol and water in the fabric resistance test. The compositions and their representative surface tensions are as follows.

<u>Liquid No.</u>	<u>Composition</u>	<u>Surface Tension</u>	
		<u>Newtons/m at 25°C</u>	<u>(dynes/cm at 25°C)</u>
1	n-heptane	19.8×10^{-3}	(19.8)
2	n-octane	21.4×10^{-3}	(21.4)
3	n-decane	23.5×10^{-3}	(23.5)
4	n-dodecane	24.7×10^{-3}	(24.7)
5	n-tetradecane	26.4×10^{-3}	(26.4)
6	n-hexadecane	27.3×10^{-3}	(27.3)

<u>Liquid No.</u>	<u>Volume % Methanol/Water</u>	<u>Surface Tension*</u>	
		<u>Newtons/m at 25°C</u>	<u>(dynes/cm at 20°C)</u>
7	65/45	30×10^{-3}	(30)
8	53/47	35×10^{-3}	(35)
9	40/60	40×10^{-3}	(40)
10	25/75	45×10^{-3}	(45)
11	21/79	50×10^{-3}	(50)
12	15/85	55×10^{-3}	(55)
13	8.5/91.5	60×10^{-3}	(60)
14	5/95	65×10^{-3}	(65)
15	0/100	73×10^{-3}	(73)

*interpolated from Handbook of Chemistry and Physics,
56th Edition, CRC Press, pp. F-42 and F-43.

The test procedure is as follows. A specimen of the covering material is placed flat on a smooth, horizontal surface. Using the method of AATCC 118-1983 except that beginning with the lowest number test liquid, 5 drops of the liquid are placed on the surface of the fabric on the side which will face the resin impregnated sheet in various locations. If three of the five drops wick into the fabric within 60 seconds, the liquid of the next higher surface energy is used. When at least 3 drops remain on the fabric surface the apparent surface tension is recorded as the range of the last two liquids.

A preferable surface energy has been determined to be 15×10^{-3} to 40×10^{-3} Newtons per meter (15 to 40 dynes per centimeter) and more preferably less than 30×10^{-3} Newtons per meter (30 dynes per centimeter) for the tested polyurethane resins.

The liquid curable compound will not leak through the envelope to cause the exterior surface of the article to become sticky or otherwise contaminated with the curable compound. A benefit thus obtained by the orthopedic article of this application is that the curable compound does not leak through the envelope and transfer to the skin of the person who applies the cast and/or the patient, where it could become firmly bonded to the skin.

An advantage of the orthopedic splinting and casting article of this invention is the high porosity which allows the injured limb to breath. The porosity of the water permeable envelope is tested using a W & L.E. Gurley Densometer Model 4110. (Troy, NY). A Gurley-Teledyne sensitivity meter (Cat. No. 4134/4135) is used (only for calibration). An Engler Instruments Co. Model 605 timer is used to record the porosity as the time in sec. to pass 100cc of air through a 2.865 cm diameter (6.452 cm²) piece of the envelope at 23.3-24.4°C and 50% relative humidity. Both single and double layers are tested in some cases. The results appear below:

	<u>Envelope Material (sec)</u>	<u>POROSITY</u>	
		<u>Single layer (sec)</u>	<u>Double layer</u>
5	Elastoflex P, 0.0381 mm thickness	Greater than 300 secs (almost no flow)	
	Adhesive-backed polyurethane foam	10.5	
10	MSO3	0.2	0.3
	MSO3 containing 2.5% FC-270	0.2	0.25
15	MSO3 containing 0.5% FC-214	0.3	0.8
	MSO3 containing 0.25% FC-214	0.3	0.7
20	MSO3 containing 1.0% FC-214	0.25	0.6
	MSO3 containing 2.0% FC-214	0.3	0.8
25	MSO3 containing 2.5% FC-461	0.2	0.5
30	MSO3 containing 2.5% FC-828	0.25	0.7
	MSO3 containing 0.25% FC-232	0.25	0.9
35	MSO3 containing 0.50% FC-232	0.25	0.7
	MSO3 containing 2.5% FC-210	0.3	0.65
40	FC-214 Splint	1.3	-

45 Elastoflex P is a proprietary elastomeric film, available from Clopay Company, Cincinnati, OH. MSO3 is the knitted polyester stockinette onto which all the fluorochemicals listed were coated. The percentage refers to % by weight of the fluorochemical which was coated onto the MSO3 knitted polyester stockinette available from 3M Company, St. Paul, MN. FC-214 Splint is eight layers of Scotchcast™ 2 casting tape enclosed in MSO3 treated with 2% FC-214.

50 A casting splint consisting of eight layers of Scotchcast™ 2 casting tape material impregnated with a water curable urethane prepolymer and enclosed on all sides by an envelope is formed into a cylinder of 5.08 cms (two inches) inner diameter and 7.62 cms (three inches) in height as shown in Figures 5a and 5b and by sealing the ends 5 and 6 together using a room temperature vulcanizing silicone adhesive such as Dow Corning 732 multipurpose sealant. The envelope totally encases the water-curable casting material and is therefore present on both the inner and outer surfaces of the cylinder which has been formed. In Sample 1, the envelope consists of an ethylene-propylene-diene film. Sample 1 is currently sold under the name Scotchcast™ 2 Splinting System by 3M Company. In Sample 2, the envelope consists of a polyester stockinette that is treated to contain 1.25% by weight of FC-214 fluorochemical. In Sample 3, the envelope consists of a first layer of polyester stockinette and a second layer over the outside of the cylinder of an open cell urethane foam adhered to the first

layer by the adhesive backing. This envelope is also treated on the stockinette portion to contain 1.25% by weight of FC-214 fluorochemical. In Sample 4, the envelope consists of a polyester stockinette treated to contain 2.5% by weight of FC-214 fluorochemical.

A beaker containing water is sealed inside the cylinder by placing a Petri dish 10 at the open bottom and top of the cylinder and gluing the dishes to the splint using a room temperature vulcanizing silicone adhesive as described hereinabove. After the adhesive is cured, this assembly is placed in a 32 to 38°C oven and weight loss of the assembly is measured as a function of time. The weight loss of the assemblies containing fabric treated with fluorochemical (Samples 2-4) is compared to an assembly in which the film was not treated with fluorochemical (Sample 1).

The properties of Samples 1-4 are shown in Table 1.

TABLE 1

Sample	% Fluorochemical added (by weight)	Newton/m	Surface Tension (dynes/cm)
1	0	not applicable	not applicable
2	1.25	$23.5 \times 10^3 - 24.7 \times 10^3$	23.5 - 24.7
3	1.25	$23.5 \times 10^3 - 24.7 \times 10^3$	23.5 - 24.7
4	2.5	$21.4 \times 10^3 - 23.5 \times 10^3$	21.4 - 23.5

The results of the water vapor porosity test are shown in Figure 8. Figure 8 shows the grams of water vapor that are transported through the splints as a function of time. As indicated in the figure, Samples 2-4, which are porous fabrics treated with fluorochemical, transport water much more rapidly than Sample 1.

The following examples are provided to illustrate the invention and should not be considered as restrictive.

EXAMPLE 1

Tubular samples of about 15 inches in length and 3 inches in diameter of 3M™ Brand MSO3 polyester stockinette are treated with the fluorochemical formulations as listed in Table 2. The wet pick-up of a solution diluted to 2.5% solids using deionized water is between 100 and 120% by weight. Percent wet pickup is weight of a wet stockinette divided by weight of a dry stockinette multiplied by 100. Each treated stockinette is heated for one hour in an oven at 149°C and stored in a dry chamber (4% relative humidity) at a constant temperature of 24°C for about three days. Each sample contains about 2.5% by weight of the fluorochemical. These are tested by the modified version of AATCC Test Method 118-1983 described above for apparent surface energy and the results are reported in Table 2. The color of each sample is recorded. Eight layers of casting tape, each 30.5 cm in length and 7.62 cm wide, made with an isocyanate-functional water-curable resin (available from 3M Company, St. Paul, MN under the name Scotchcast™ 2 Brand casting tape) were enclosed in the treated tubular stockinette. The ends of the tube are placed in apposition and carefully heat sealed with a Vertrod Mead Model 14A-A-CAB Sealer. The casting articles were folded as shown in Figure 7, packaged and sealed in aluminum foil pouches and aged at 49°C. After two weeks the pouches are opened and the aged articles were inspected visually for color and manually for the presence of resin on the outer fabric surface. The results are shown in Table 2.

TABLE 2

Run No.	Fluorochemical Treatment	Color of Stockinet	Description of Aged Articles	Newton/m	Apparent Surface Energy Range (dyne/cm)
A	FC-214	No Change	No resin leakage	21.4×10^{-3} - 23.5×10^{-3}	(21.4 - 23.5)
B	FC-210	No Change	No resin leakage	21.4×10^{-3} - 23.5×10^{-3}	(21.4 - 23.5)
C	FC-232	No Change	No resin leakage	21.4×10^{-3} - 23.5×10^{-3}	(21.4 - 23.5)
D	FC-828	Slight Yellowing	No resin leakage	23.5×10^{-3} - 24.7×10^{-3}	(23.5 - 24.7)
E	FC-461	Slight Yellowing	No resin leakage	21.4×10^{-3} - 23.5×10^{-3}	(21.4 - 23.5)
F	untreated	Not Applicable	Visible wet out / sticky	$> 72 \times 10^{-3}$	(>72)

This example shows that with the specific stockinet and resin used, three completely satisfactory fluoro-chemical treatments were found.

EXAMPLE 2

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Samples of 3M™ Brand MSO3 polyester stockinet and commercially available cotton stockinet are treated with 1.5% and 2.5% by weight total solids aqueous solution of FC-214. This is supplied as a 30% solids solution, and hence can be diluted to obtain the desired solids content. A wet pickup of 45% was obtained for the 7.6 cm diameter cotton stockinet cylinder. The wet pickup is controlled by passing the soaked materials through a set of nip rollers. The stockinet samples are soaked in the solutions, then dried by hanging in a convection oven at 160°C for 40 minutes. The surface tension of the outside and inside surface of each stockinet is qualitatively evaluated visually after applying water and modified diphenylmethane, available from DOW Chemical under the name Isonate™ 143L. Both the inside and outside surfaces repelled these chemicals, i.e., droplets of these liquid chemicals remained beaded up on the surface and did not wick into the fabric. Untreated samples were wetted by both water and Isonate 143L.

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EXAMPLE 3

Samples of nonwoven sheets of commercially available spun-laced, hydroentangled nonwoven polyester fabrics Sontara 8000, 8005 and 8010 (available from du Pont, Wilmington, DE) are treated with commercially available FC-214. The FC-214 is diluted to 2% solids with water. The fabrics are soaked in the solution, run through a nip roller, re-soaked, and again run through the nip roller to provide a substantially uniform 100% wet pickup. Untreated samples are soaked in water. All of the samples are dried as described in Example 2 and the surface tension of each sample qualitatively tested as in Example 2. The treated samples have significantly reduced surface tension compared to the untreated samples. This is shown by the fact that water and Isonate™ 143L would not wet the treated fabric but the untreated fabric is wetted. Splints are made from these samples and described in Example 1 and are aged at 24°C for 2 months without any detectable resin leakage. Control samples which were not treated showed visible resin wet-out after 4 weeks and were sticky.

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EXAMPLE 4

Two casting splints 7.62 cms (3 inches) in width are made using a commercially available polyethylene terephthalate terry cushion stockinet (available from Balfour, Inc., Rockwood, TN) are treated with a solution of FC-214 diluted to 2.5% solids (120% pickup) to encase eight layers of Scotchcast™ 2 Brand Casting Tape. The ends of the stockinets are heat sealed to form a complete closure. One side of each splint is covered with a 7.62 cm wide strip of water-impervious Scotch™ Brand polyester tape No 355-G clear tape (available from 3M Company, St. Paul, MN). The splints are dipped in water to initiate curing, removed from the water, then the vinyl tape is removed to expose a dry surface. The dried surface is applied to the skin and is comfortable and not damp.

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EXAMPLE 5

Two casting splints 7.62 cm in width and 35.56 cm long are made using the stockinet material and casting tape of Example 4 which are heat sealed. A 7.62 cm wide, 0.476 cm thick strip of adhesive backed polyurethane foam of equal length to the splint is glued at each end to the ends of the splint with 3M™ brand hot melt adhesive. The splint is dipped in water while holding the foam section of the splint out of the water. The splint is removed from the water. Excess water is removed by hand squeezing, the adhesive side of the foam is applied to the splint and the dry foam side of the assembly is applied to the skin as the assembly is used as a splint. The skin area is comfortable and not damp.

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EXAMPLE 6

In order to obtain quantitative measurements of the repellency of treated stockinets of the instant invention, 7.62 cm wide and 5.08 cm long sections of treated fabrics which are made by the method of Example 1 are evaluated using the modified version of AATCC Test Method 118-1983 described above for apparent surface energy as shown in Table 3.

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TABLE 3

Run	Stockinet Fabric Treatment*	Newtons/m	Surface Energy Range (Dynes/cm)
1A	FC 232, 0.25%	27.3×10^{-3} to 29.6×10^{-3}	(27.3 to 29.6)
2A	FC 232, 0.50%	26.4×10^{-3} to 27.3×10^{-3}	(26.4 to 27.3)
3A	FC 232, 1.0%	23.5×10^{-3} to 24.7×10^{-3}	(23.5 to 24.7)
4A	FC 232, 2.0%	21.4×10^{-3} to 23.5×10^{-3}	(21.4 to 23.5)
5A	FC 214, 0.25%	24.7×10^{-3} to 26.4×10^{-3}	(24.7 to 26.4)
6A	FC 214, 0.50%	24.7×10^{-3}	(24.7)
7A	FC 214, 1.0%	23.5×10^{-3} to 24.7×10^{-3}	(23.5 to 24.7)
8A	FC 214, 2.0%	21.4×10^{-3} to 23.5×10^{-3}	(21.4 to 23.5)
9A	Dow C 20563 Silicone, 2%	Between 27.3×10^{-3} and 30×10^{-3}	(Between 27.3 and 30)
10A	General Electric 5540 98 Silicon, 2.4%	Between 27.3×10^{-3} and 30×10^{-3}	(Between 27.3 and 30)
11A	Orthoglass Rollform Splint	greater than 72×10^{-3}	(greater than 72**)
12A	Untreated Stockinet	greater than 72×10^{-3}	(greater than 72**)
13	FC 270, 25%	24.7×10^{-3} to 26.4×10^{-3}	(24.7 to 26.4)

*All percents are grams of solid per gram of fabric times 100
 **Wetted by distilled water

Runs 9A and 10A provided splints which yellowed. After one week aging at 49°C neither splint showed resin leakage. After 19 days at 49°C splint 9A was not sticky but splint 10A was sticky.

Claims

1. An orthopedic article adapted to immobilize a body part comprising (a) a flexible substrate having opposing surfaces impregnated with a liquid curable compound, and (b) a cover comprising a flexible sheet and a fluorochemical compound or polymer containing one or more fluoroaliphatic radicals or perfluoroaliphatic groups or a silicone capable of imparting water repellency disposed on the surfaces that is permeable to water and impermeable to the said liquid curable compound.
2. An article according to Claim 1, wherein the cover comprises a layer of a fluorochemical compound or polymer containing one or more fluoroaliphatic radicals or perfluoroaliphatic groups or a silicone capable of imparting water repellency sandwiched between the substrate and the flexible sheet.
3. An article according to either of Claims 1 and 2, wherein the cover has an apparent surface energy of less than 30×10^{-3} Newtons per meter (30 dynes per centimeter) and a porosity of less than 0.5 seconds.
4. An article according to any one of Claims 1 and 2, wherein the apparent surface energy of the cover ranges from 15×10^{-3} to 40×10^{-3} Newtons per meter (15 to 40 dynes per centimeter) and the cover has a porosity less than 1.0 second.
5. An article according to any one of Claims 1 to 4, wherein the flexible sheet comprises a knitted, woven, or non-woven fabric treated with the said fluorochemical compound or polymer containing one or more fluoroaliphatic radicals or perfluoroaliphatic groups or said silicone capable of imparting water repellency.
6. An article according to any one of Claims 1 to 5, wherein the liquid curable compound is a water-curable isocyanate-terminated prepolymer resin.
7. An article according to any one of Claims 1 to 6, further comprising a foam layer disposed between the cover and the substrate on one surface of the substrate, wherein said foam layer is adapted to contact the body part to be immobilized.
8. An article according to any one of Claims 1 to 7, wherein the amount of said fluorochemical compound or polymer containing one or more fluoroaliphatic radicals or perfluoroaliphatic groups or said silicone capable of imparting water repellency is from 0.01 to 10% by weight of the flexible sheet.
9. An article according to Claim 8, wherein the amount of said fluorochemical compound or polymer containing one or more fluoroaliphatic radicals or perfluoroaliphatic groups or said silicone capable of imparting water repellency is from 0.25 to 5% by weight of the flexible sheet.
10. An article according to any one of Claims 1 to 9, wherein the cover comprises a sealed envelope encasing the substrate.
11. An article according to any one of Claims 1 to 10, wherein the substrate comprises a laminate of woven or non-woven webs.
12. An article according to any one of Claims 1 to 11, wherein the curable compound has been cured.
13. A method of making the orthopedic article of any one of Claims 1 to 12 comprising the steps of (a) impregnating a flexible substrate having opposing surfaces with a liquid curable compound, and (b) applying a cover comprising a flexible sheet and a fluorochemical compound or polymer containing one or more fluoroaliphatic radicals or perfluoroaliphatic groups or a silicone capable of imparting water repellency to the surfaces that is permeable to water and impermeable to the said liquid curable compound.
14. A method according to Claim 13 of forming a final shaped article comprising the steps of (a) activating the said liquid curable compound, (b) shaping the article of any one of Claims 1 to 12 to conform to a body part, and (c) allowing the said liquid curable compound to cure.
15. A method according to Claim 14, wherein the said liquid curable compound is activated by soaking the article in water.

Substrat
Abdeckung
Bohne R.

Patentansprüche

1. Orthopädischer Gegenstand, der zum Ruhigstellen eines Körperteils geeignet ist, mit (a) einem flexiblen Substrat, das einander entgegengesetzte Oberflächen besitzt, die mit einer härtbaren flüssigen Verbindung imprägniert sind, und (b) einer auf den Oberflächen angeordneten, für Wasser durchlässigen und für die härtbare flüssige Verbindung undurchlässigen Abdeckung, die ein flexibles Blatt und eine Fluorverbindung oder ein Polymer, die bzw. das ein oder mehrere fluoraliphatische Radikale oder perfluoraliphatische Gruppen besitzt, oder ein wasserabweisendmachendes Silicon enthält.
2. Gegenstand nach Anspruch 1, dadurch gekennzeichnet, daß die Abdeckung eine zwischen dem Substrat und dem flexiblen Blatt angeordnete Schicht aus einer Fluorverbindung oder einem Polymer, die bzw. das ein oder mehrere fluoraliphatische Radikale oder perfluoraliphatische Gruppen besitzt, oder ein wasserabweisendmachendes Silicon enthält.
3. Gegenstand nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Abdeckung eine scheinbare Oberflächenenergie von weniger als $30 \cdot 10^{-3}$ Newton/m (30 Dyn/cm) und eine Porosität von weniger als 0,5 s hat.
4. Gegenstand nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Abdeckung eine scheinbare Oberflächenenergie der im Bereich von $15 \cdot 10^{-3}$ bis $40 \cdot 10^{-3}$ Newton/m (15 bis 40 dyn/cm) und eine Porosität unter 1,0 s hat.
5. Gegenstand nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das flexible Blatt wenigstens teilweise aus einem einem Textilstoff in Form einer Maschenware oder eines Gewebes oder eines Vliesstoffes besteht und der Textilstoff mit der Fluorverbindung oder dem Polymer, die bzw. das eine oder mehrere fluoraliphatische Radikale oder perfluoraliphatische Gruppen besitzt, oder dem wasserabweisendmachenden Silicon behandelt ist.
6. Gegenstand nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die härtbare flüssige Verbindung ein mit Wasser härtbares Vorpolymerharz mit endständigem Isocyanat ist.
7. Gegenstand nach einem der Ansprüche 1 bis 6, der ferner zwischen der Abdeckung und einer Oberfläche des Substrats eine Schaumstoffschicht besitzt, die zur Anlage an dem ruhigzustellenden Körperteil geeignet ist.
8. Gegenstand nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Menge der Fluorverbindung oder des Polymers, die bzw. das eine oder mehrere fluoraliphatische Radikale oder perfluoraliphatische Gruppen besitzt, oder des wasserabweisendmachenden Silicons 0,01 bis 10 Gew.-% des flexiblen Blattes beträgt.
9. Gegenstand nach Anspruch 8, dadurch gekennzeichnet, daß die Menge der Fluorverbindung oder des Polymers, die bzw. das eine oder mehrere fluoraliphatische Radikale oder perfluoraliphatische Gruppen besitzt, oder des wasserabweisendmachenden Silicons 0,25 bis 5 Gew.-% des flexiblen Blattes beträgt.
10. Gegenstand nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß die Abdeckung wenigstens teilweise aus einer dichtverschlossenen Hülle besteht, die das Substrat umschließt.
11. Gegenstand nach einem der Ansprüche 1 bis 10, dadurch gekennzeichnet, daß das Substrat wenigstens teilweise aus einem Schichtstoff aus gewebtem Gewebe- und Vliesstofflagen besteht.
12. Gegenstand nach einem der Ansprüche 1 bis 11, dadurch gekennzeichnet, daß die härtbare Verbindung gehärtet ist.
13. Verfahren zum Herstellen des orthopädischen Gegenstandes nach einem der Ansprüche 1 bis 12, mit folgenden Schritten: (a) ein einander entgegengesetzte Oberflächen besitzendes, flexibles Substrat wird mit einer härtbaren flüssigen Verbindung imprägniert und (b) auf die Oberflächen wird eine für Wasser durchlässige Abdeckung aufgetragen und für die härtbare flüssige Verbindung durchlässige ist ein flexibles Blatt und eine Fluorverbindung oder ein Polymer, die bzw. das eine oder mehrere fluoraliphatische Radikale oder perfluoraliphatische Gruppen besitzt, oder ein wasserabweisendmachendes Silicon enthält.

14. Verfahren nach Anspruch 13 zum Herstellen eines fertigen Gegenstandes mit folgenden Schritten: (a) die härtbare flüssige Verbindung wird aktiviert, (b) der Gegenstand nach einem der Ansprüche 1 bis 12 wird zu seiner Anpassung an einen Körperteil verformt und (c) die härtbare flüssige Verbindung wird erhärten gelassen.

15. Verfahren nach Anspruch 14, dadurch gekennzeichnet, daß zum Aktivieren der härtbaren flüssigen Verbindung der Gegenstand in Wasser gehalten wird.

Revendications

1. Article orthopédique destiné à immobiliser une partie du corps, comprenant (a) un substrat souple ayant des surfaces opposées imprégnées d'un composé liquide durcissable et (b) un recouvrement, comprenant une feuille souple et un composé ou polymère fluorés contenant un ou plusieurs radicaux fluoroaliphatiques ou groupes perfluoroaliphatiques ou une silicone capables de conférer un caractère hydrofuge, disposé sur les surfaces, qui est perméable à l'eau et imperméable audit composé liquide durcissable.
2. Article selon la revendication 1, dans lequel le recouvrement comprend une couche d'un composé ou polymère fluorés contenant un ou plusieurs radicaux fluoroaliphatiques ou groupes perfluoroaliphatiques ou d'une silicone capables de conférer un caractère hydrofuge, intercalée entre le substrat et la feuille souple.
3. Article selon la revendication 1 ou 2, dans lequel le recouvrement a une énergie superficielle apparente inférieure à 30×10^{-3} necton par mètre (30 dynes par centimètre) et une porosité inférieure à 0,5 seconde.
4. Article selon l'une quelconque des revendications 1 et 2, dans lequel l'énergie superficielle apparente du recouvrement se situe dans la gamme de 15×10^{-3} à 40×10^{-3} necton par mètre (15 à 40 dynes par centimètre) et le recouvrement a une porosité inférieure à 1,0 seconde.
5. Article selon l'une quelconque des revendications 1 à 4, dans lequel la feuille souple comprend une étoffe tricotée, tissée ou non tissée, traitée avec ledit composé ou polymère fluorés contenant un ou plusieurs radicaux fluoroaliphatiques ou groupes perfluoroaliphatiques ou ladite silicone capables de conférer un caractère hydrofuge.
6. Article selon l'une quelconque des revendications 1 à 5, dans lequel le composé liquide durcissable est une résine de prépolymère à terminalson isocyanate durcissable par l'eau.
7. Article selon l'une quelconque des revendications 1 à 6 comprenant de plus une couche de mousse disposée entre le recouvrement et le substrat sur une surface du substrat, ladite couche de mousse étant conçue pour venir en contact avec la partie du corps à immobiliser.
8. Article selon l'une quelconque des revendications 1 à 7, dans lequel la proportion dudit composé ou polymère fluorés, contenant un ou plusieurs radicaux fluoroaliphatiques ou groupes perfluoroaliphatiques, ou de ladite silicone, capables de conférer un caractère hydrofuge, est de 0,01 à 10 % du poids de la feuille souple.
9. Article selon la revendication 8, dans lequel la proportion dudit composé ou polymère fluorés, contenant un ou plusieurs radicaux fluoroaliphatiques ou groupes perfluoroaliphatiques, ou de ladite silicone, capables de conférer un caractère hydrofuge, est de 0,25 à 5 % du poids de la feuille souple.
10. Article selon l'une quelconque des revendications 1 à 9, dans lequel le recouvrement comprend une enveloppe fermée hermétiquement enfermant le substrat.
11. Article selon l'une quelconque des revendications 1 à 10, dans lequel le substrat comprend un stratifié de feuilles tissées ou non tissées.
12. Article selon l'une quelconque des revendications 1 à 11, dans lequel le composé durcissable a été durci.
13. Procédé pour préparer l'article orthopédique de l'une quelconque des revendications 1 à 12 comprenant les étapes de (a) imprégnation d'un substrat souple ayant des surfaces opposées avec un composé liquide

durcissable et (b) application d'un recouvrement comprenant une feuille souple et un composé ou polymère fluorés, contenant un ou plusieurs radicaux fluoroaliphatiques ou groupes perfluoroaliphatiques, ou une silicone, capables de conférer un caractère hydrofuge aux surfaces, qui est perméable à l'eau et imperméable audit composé liquide durcissable.

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14. Procédé selon la revendication 13 pour former un article façonné final comprenant les étapes consistant à (a) activer ledit composé liquide durcissable, (b) façonner l'article de l'une quelconque des revendications 1 à 12 pour qu'il s'adapte à une partie du corps et (c) laisser durcir ledit composé liquide durcissable.
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15. Procédé selon la revendication 14, dans lequel ledit composé liquide durcissable est activé par trempage de l'article dans l'eau.
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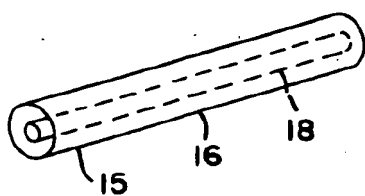
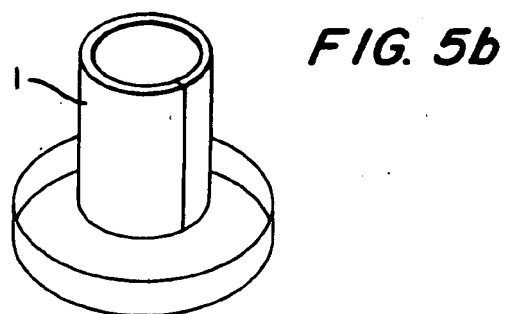
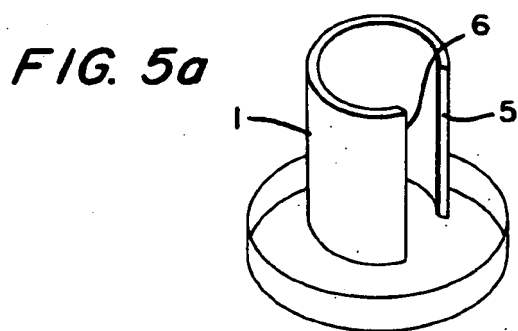
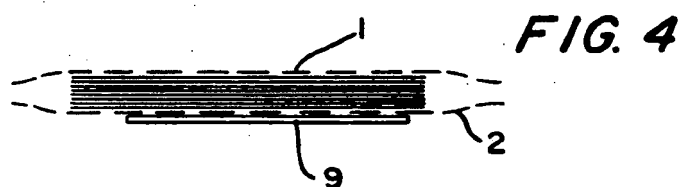
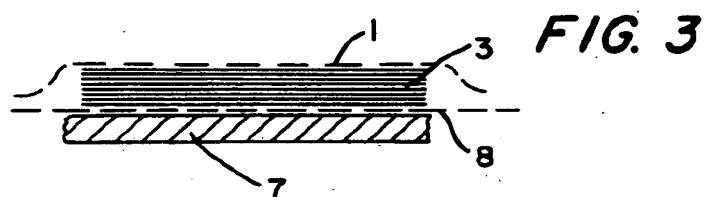
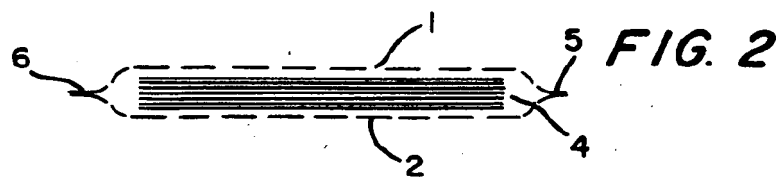
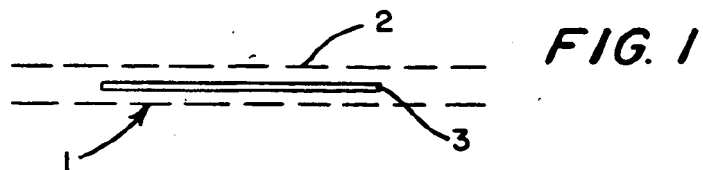
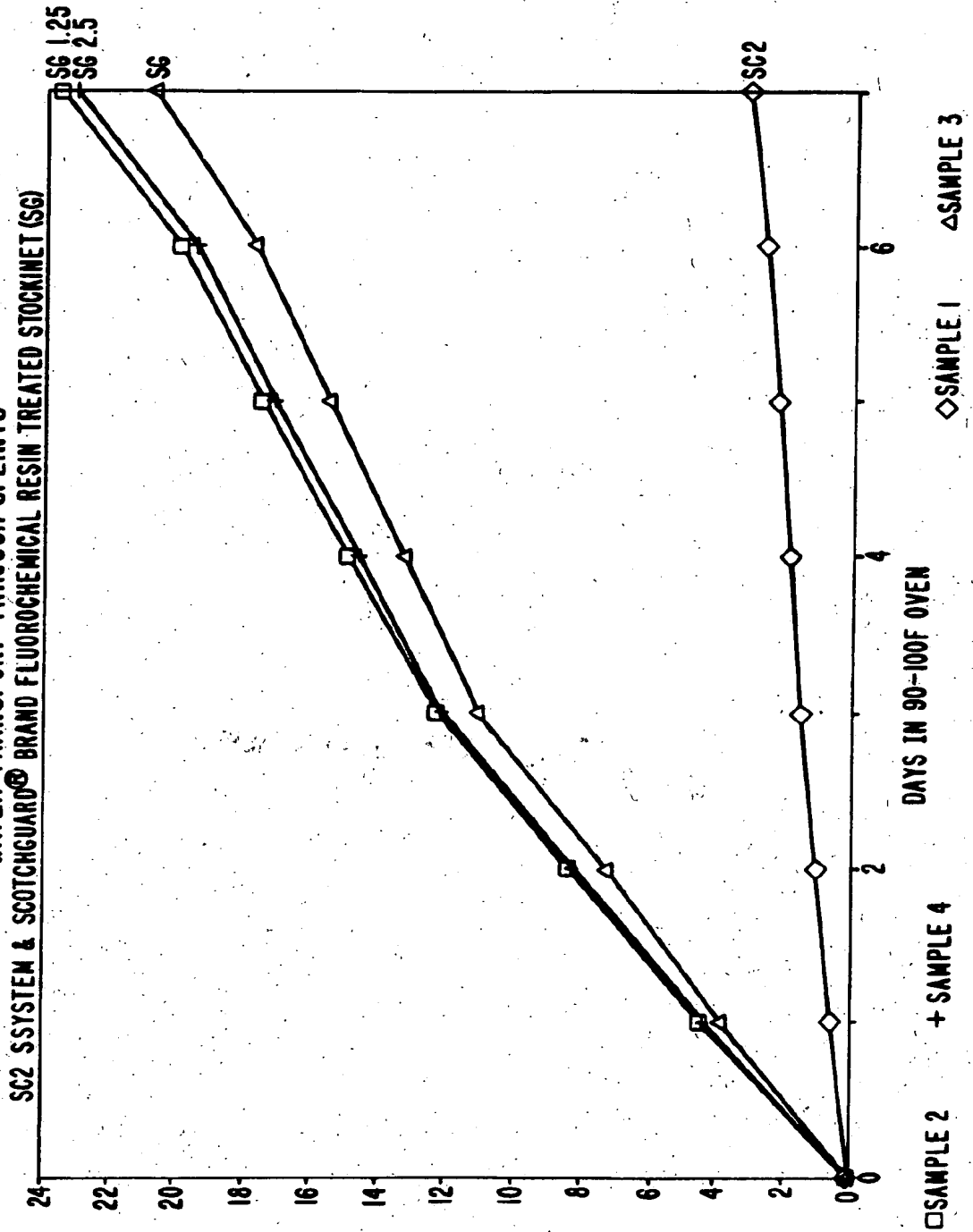


FIG. 8

WATER TRANSPORT THROUGH SPLINTS



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